



Short communication

The effect of high anionomer loading with silver nanowire catalysts on the oxygen reduction reaction in alkaline environment



Adam J. Lemke*, Alexander W. O'Toole, Richard S. Phillips, Eric T. Eisenbraun

SUNY College of Nanoscale Science and Engineering, Albany, NY, United States

HIGHLIGHTS

- We looked at the use of silver nanowires in combination with anionomer.
- We investigated the effect of high anionomer loadings on the ORR pathway.
- We used Koutecky–Levich analysis to determine the average n value for samples.

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ABSTRACT

The effect of ionomer content on the oxygen kinetics in fuel cells and metal-oxide batteries was investigated by varying ionomer loading with constant loadings of a silver nanowire catalyst. Silver nanowire inks were produced in which commercially available anionomer solution constituted 10, 25, 40, 50, and 75% of the total ink volume. Constant loadings of Ag nanowire catalyst were then deposited onto glassy carbon electrodes by varying the amount of ink deposited. These were then used in rotating disc electrode (RDE) experiments using a 0.1 M KOH electrolyte solution. From these experiments, using ORR polarization curves and Koutecky–Levich analysis, it was found that not only did the anionomer loading affect the total activity (given a constant Ag nanowire loading) but, that the anionomer content also had an impact upon the apparent kinetic limited current as well as whether the ORR proceeded through the $2e^-$ or $4e^-$ pathway. Although the total activity declined with very high anionomer loadings, the ORR appeared to proceed more through the $4e^-$ pathway with increased anionomer content.

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1. Introduction

The oxygen reduction reaction (ORR) is an electrochemical reaction of great importance due to the central role that it plays in energy technologies such as fuel cells and metal-air batteries. The ORR is also a very complex reaction that is not fully understood and is indeed the primary limiting reaction in these technologies, making it an area of intense study [1,2]. The kinetics of the ORR result in a high overpotential and a slowing down of the overall reaction of the system. There are two overall pathways through which ORR can proceed: a four-electron ($4e^-$) pathway in which four electrons are exchanged in one step, and a two-electron ($2e^-$) pathway in which there is an initial reduction of oxygen, with an exchange of two electrons, to peroxide which must then be reduced again by an additional two electrons in a subsequent step [1]. This is the case in both acidic and alkaline environments, despite

differences in the details of how the reactions proceed in each type of environment. Because the formation of peroxide as a secondary intermediate results in a loss of efficiency, as well as the fact that the peroxide can corrode the electrode material, it is desirable to promote the $4e^-$ pathway over the $2e^-$ pathway.

The most commonly used air electrode catalyst material for oxygen catalysis in such systems is Pt, whose rarity and cost create a significant economic hurdle impeding the more widespread use of these technologies [3,4]. Much effort has thus been devoted to trying to devise ways to reduce Pt loading while maintaining oxygen activity. In this regard, there is a significant advantage associated with alkaline systems, in that they are well known to allow for a much wider choice of catalyst materials for ORR than do acidic systems and help to promote the $4e^-$ pathway. This is due to the outer sphere reactions that take place in alkaline systems which effectively allows electrons from the electrode to tunnel to the O_2 reactant in solution, instead of requiring the oxygen molecule to first adsorb to an active site prior to reduction [5–7]. This permits a wider range of materials to act as oxygen catalysts promoting the four-electron pathway.

* Corresponding author.

E-mail addresses: alemke@albany.edu (A.J. Lemke), aotoole@albany.edu (A.W. O'Toole), rphillips@albany.edu (R.S. Phillips), eeisenbraun@albany.edu (E.T. Eisenbraun).

Because of this there is an interest in the use of oxygen catalysts in alkaline systems for use in technologies such as metal-air batteries and alkaline fuel cells. Silver makes for an intriguing candidate as an alternative catalyst material to Pt in alkaline systems. Silver has been previously shown to promote the four-electron pathway, with minimal peroxide production (indicative of the two-electron pathway), with an activity near that of Pt in alkaline systems [8]. Single crystal (110) Ag has exhibited the highest ORR activity, which is due to its having the lowest apparent activation energy of the three single crystal surfaces, albeit Ag shows lower structural sensitivity than Pt [9]. Given that silver is a fraction of the cost of platinum (between 2007 and 2011 the price per unit weight of silver was less than 2% that of platinum) [10], it is an economically attractive catalyst material alternative for use in alkaline systems. Also, silver is the most conductive of metals and can potentially be used as its own support (i.e. eliminating the need for a potentially unstable support structure to conduct electrons).

Another important issue regarding oxygen electrodes is the stability of the support material. In both fuel cells and metal-air batteries carbon is the most widely used catalyst support material. Unfortunately, carbon tends to corrode and degrade over time at the voltages under which these systems operate [11]. Therefore it may be desirable to eliminate the carbon support structure entirely.

It is also important to note the use of polymer electrolytes in fuel cells. Polymer electrolytes have already been in use for some time in acidic systems, notably in proton exchange membrane (PEM) fuel cells. In these systems an ion-carrying polymer, also known as an “ionomer” is used as an electrolyte, which allows for the transport of the ions in the electrochemical device. In the case of PEM fuel cells, the polymer allows for the transport of H^+ ions from one electrode to the other. There do also exist polymer electrolytes that carry OH^- ions instead of protons, termed “anionomers” which would be suitable for alkaline systems. It has been shown previously that the use of anionomer membranes in alkaline systems can be effective in preventing the formation of carbonate [12]. This is important because atmospheric carbon dioxide can react with the electrolyte to form carbonate, resulting in poisoning of the system by reducing the ionic conductivity of the electrolyte and clogging pores when it deposits [13,14].

In this paper the use of silver nanowires in combination with anionomer as an ORR catalyst in alkaline systems is investigated. Structured silver catalysts, used without any additional support material, were examined and their performance was measured using a rotating disc electrode (RDE) in combination with various amounts of anionomer in a fixed amount of catalyst ink. By producing inks with higher-than-normal ionomer content and varying the ratio of the ionomer solution to the total volume of the produced inks, it was possible to have constant loadings of Ag nanowire catalysts with large, but variable quantities of anionomer. In doing so it became possible to investigate how anionomer loading affects the ORR kinetics, which take place at the disc electrode with constant loadings of Ag nanowire catalyst.

2. Experimental

2.1. Preparing the Ag nanowire inks

For this experiment it was important to use Ag with a high surface area in order to try and maximize active sites; therefore Ag nanowires were utilized. A solution of commercially available Ag nanowires in isopropanol purchased from Blue Nano Inc. was used. The nanowires were 90 nm in diameter and several microns in length and were in a concentration of 10 mg ml^{-1} in solution.

A series of simple inks were prepared by combining the Ag nanowires solution with a solution of the commercially available

ionomer AS-4 which was purchased from Tokuyama Corp. The AS-4 anionomer came in a 90–98% propanol solution from the manufacturer. The Ag nanowire and anionomer solutions were combined to produce inks such that 10, 25, 40, 50, 60, 75 and 90 vol% of the resulting ink was anionomer solution. These inks were sonicated for one hour prior to deposition in order to ensure good dispersion.

The inks were then deposited onto the glassy carbon (GC) disc electrode for 30, 75, 120, 150, 180 and 225 μg loadings of Ag NWs, each with varying loadings of anionomer. This was done by varying the total volume of the ink deposited between 10 and 30 μl so as to have the total mass loading of the Ag nanowires be the same for each of the inks that were used. Applications less than 10 μl did not result in good coverage of the GC electrode, and applications more than 30 μl resulted in the droplet breaking, thus defining the workable volume range of the deposited ink droplets. This was done for several different mass loadings of Ag nanowires, which are shown in Table 1. After deposition, the inks were dried in an oven at 60°C for 30 min. Once dried, the GC electrode could then be used in the rotating ring disc electrode (RRDE) setup.

2.2. Electrochemical characterization

For the RDE measurements, a Pine Research Instrumentation system was used, including an AFCBP1 Bipotentiostat and an AFMSRCE Modulated Speed Rotator. The bipotentiostat was controlled via computer using the AfterMath software that was included with the RRDE system. For all of the RRDE experiments a 0.1 M KOH solution was used for the electrolyte solution. For cyclic voltammetry (CV) measurements, the KOH solution was first purged with 99.999% purity Ar for 30 min to ensure that the electrolyte was deaerated prior to running the CVs. The GC disc with the deposited ink would then be electrochemically cleaned by cycling the potential at 200 mV s^{-1} for an extended period until the CV stabilized. Cyclic voltammograms were run at 10, 20, 30, 40 and 50 mV s^{-1} .

In addition to the Ag NW inks, the plain, uncoated glassy carbon electrode was also subjected to the same electrochemical characterization. For comparison, 10 μl of the anionomer solution, without any Ag NWs, was deposited onto the GC electrode and dried. This too was then tested. An ink made from 20 wt% commercial Pt/C was also used as a standard. The catalysts powder was dispersed in a solution with 0.5 vol% anionomer at a ratio of 2 mg ml^{-1} . The ink was then sonicated to ensure good dispersion. Then 30 μl were pipetted onto the glassy carbon electrode and dried for a loading of 60 μg .

For ORR polarization experiments the KOH solution was purged with 99.999% purity O_2 for 30 min to ensure that the electrolyte was oxygenated. The potential on the GC electrode would then be swept from 0.1 to -1.2 V at rotation rates of 100, 400, 900 and 1600 rpm. All potentials are referenced to a saturated calomel electrode (SCE) which was calibrated to be $+0.241 \text{ V}$ from the standard hydrogen electrode (SHE).

Table 1

Loadings of Ag nanowire inks for various volume percents of anionomer solution of total ink volume.

Ag NW loading	90 vol%	75 vol%	60 vol%	50 vol%	40 vol%	25 vol%	10 vol%
30 μg	30 μl	12 μl					
75 μg		30 μl	18.75 μl	15 μl	12.5 μl	10 μl	
120 μg			30 μl	24 μl	20 μl	16 μl	
150 μg				30 μl	25 μl	20 μl	
180 μg					30 μl	24 μl	20 μl
225 μg						30 μl	25 μl

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows a series of cyclic voltammograms which were taken from the sample wherein 30 μl of the 50 vol% anionomer ink was deposited, resulting in a Ag nanowire loading of 150 μg . These CVs are typical of the results from the Ag nanowire/anionomer inks that were prepared. The general shape of the CVs shown here are consistent with those seen in literature with Ag catalysts in alkaline systems [15–17]. As the potential is swept in the positive direction, two broad anodic peaks can be seen at around 0.2 and 0.3 V (vs. SCE) that overlap to a large extent, making it somewhat difficult to distinguish the two. It is generally believed that these peaks correspond to the oxidation of metallic Ag to Ag_2O involving a dissolution of the metallic silver and the formation of AgOH as an intermediate. Sweeping in the negative potential direction, a sharp cathodic peak centered near 0.1 V can be seen, which corresponds to the reduction of Ag_2O back to metallic Ag [13–15].

For comparison, Fig. 2 shows two CV curves, both recorded at a scan rate of 50 mV s^{-1} . This figure shows the CVs for an uncoated glassy carbon (GC) electrode and a GC electrode that has had 10 μl of the anionomer solution deposited on it. It can be seen that currents for both of these CVs are considerably lower than those of the sample with Ag NWs, and furthermore are lacking any characteristic peaks. This indicates that the peaks seen with the Ag NWs deposited on the GC electrode are indeed attributable to the silver.

3.2. ORR polarization

To perform ORR studies, while the 0.1 M KOH electrolyte is oxygenated, the potential on the disc electrode is swept in the negative direction to reducing potentials, while measuring the resulting current at the disc. Fig. 3 shows a typical series of ORR polarization curves for the Ag nanowire/anionomer inks that were deposited on the GC electrode. As the potential is swept in the negative direction, the current increases with increasing (oxygen reduction) activity at the GC disc electrode, until it levels off in the diffusion-limited region. As can be seen, the currents tend to increase with increasing rotation rate up until around 1600 rpm then stabilize. This is likely due to internal diffusion limiting factors within the catalyst layer deposited on the GC electrode itself [18]. This is to be expected as the increasing rotation rate will increasingly overcome the diffusion limitations of the oxygen reduction current. This data was collected for all of the various samples of Ag nanowire/anionomer inks that were produced and deposited onto the GC disc electrodes.

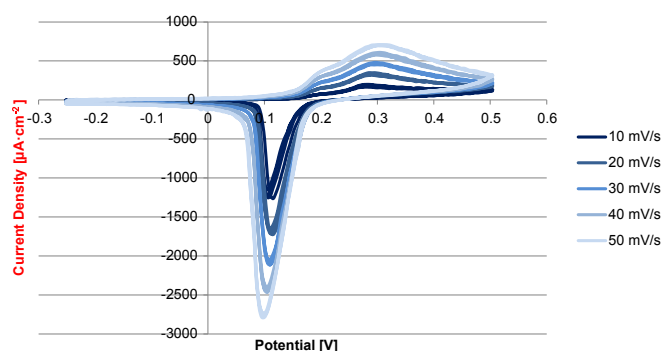


Fig. 1. Cyclic voltammograms of 30 μl of 50 vol% anionomer ink for a total Ag nanowire loading of 150 μg .

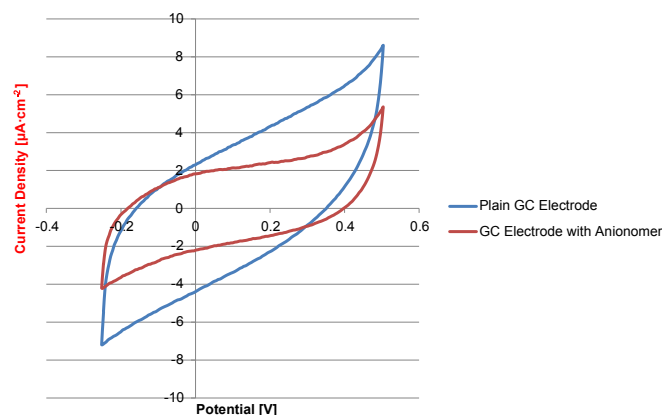


Fig. 2. Cyclic voltammograms of plain glassy carbon electrode and GC electrode coated with 10 μl anionomer solution.

Fig. 4 shows the polarization curves for both an uncoated glassy carbon electrode and a GC electrode with 10 μl of anionomer solution deposited on it, as well as the GC electrode with the Pt/C, all taken at a rotation speed of 1600 rpm. From this figure it is apparent that the addition of the anionomer has greatly reduced the diffusion limiting current relative to the clean GC electrode. This may be due to the low conductivity of the anionomer and its being deposited in a large quantity. Comparing with the diffusion limiting current achieved at 1600 rpm with the Ag NW deposited electrode, it is seen that the still-high anionomer content again reduces the current, but the Ag NWs partially overcome this effect.

Using the diffusion limiting currents reached at the highest rotation rates, a specific current density per mass of deposited catalyst was calculated for each of the samples Ag NW samples. In Fig. 5 shows the current densities are plotted against the anionomer content of the inks for various constant loadings of Ag nanowires. It can be seen that for all of the Ag NW loadings, the specific current density decreases with increasing anionomer content. Although not shown in the figure, the specific current density was also calculated for the Pt/C sample and was found to be 18 mA mg^{-1} .

There are similarities between the ORR reaction pathways in both acidic and alkaline environments, such that an overall scheme that applies to both conditions can be proposed. Under this scheme, the first step is the adsorption of an oxygen molecule onto a catalyst active site. The adsorbed oxygen molecule is then reduced either reduced directly in a four-electron transfer to water, or else is reduced to adsorbed hydrogen peroxide $\text{H}_2\text{O}_{2, \text{ad}}$ as an intermediate via a two electron transfer. The adsorbed hydrogen peroxide can then be reduced to water by an additional two electrons, or else can desorb from the active site and go into solution [1,6,19,20].

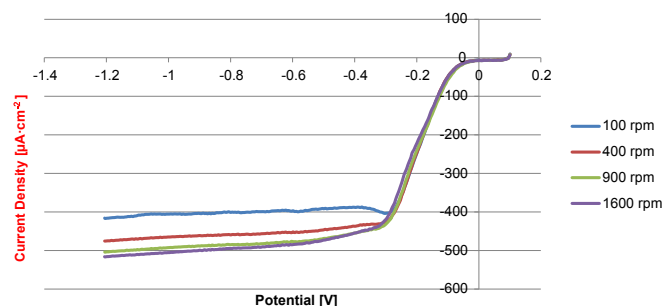


Fig. 3. ORR polarization curves for 30 μl of 50 vol% anionomer ink for a total Ag nanowire loading of 150 μg .

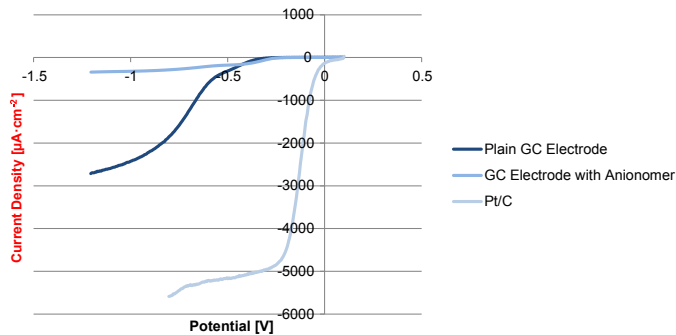


Fig. 4. ORR polarization curves for plain glassy carbon electrode and GC electrode coated with 10 µl of anionomer solution.

In the reduction of oxygen, the rate-limiting step is believed to be the addition of the first electron to the O₂ molecule to form a superoxide radical [21,22]. In what is referred to as an inner sphere reaction, the oxygen molecule is first adsorbed to an active site on the catalyst surface. This would thus necessarily take place within the inner Helmholtz plane (IHP). Alternatively, the formation of the superoxide radical can occur in what is called an outer sphere reaction. In an outer sphere reaction, a hydrogen bond is formed between a hydroxyl species adsorbed to the catalyst surface (in the IHP) and a water molecule that is solvating an oxygen molecule in the outer Helmholtz plane (OHP). This hydrogen bond essentially allows an electron from the conductive catalyst to tunnel to the solvated oxygen molecule and reduce it to a superoxide radical. While in principle the outer sphere reaction can occur in both acidic and alkaline environments, the superoxide radical is more unstable in acidic environments due to an increased rate of proton transfer, making the outer sphere reaction a viable pathway only in alkaline environments [3].

3.3. Koutecky–Levich analysis

With the ORR polarization curves collected from the samples, it was then possible to perform Koutecky–Levich analysis [2,23]. In the basic Levich equation, the description of the diffusion-limited current is as follows

$$i_d = 0.62 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C \quad (1)$$

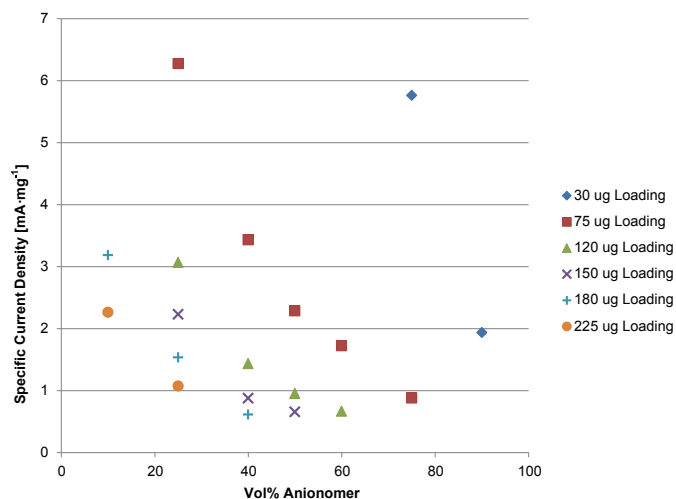


Fig. 5. Specific current densities versus vol% of anionomer in ink for various Ag nanowire loadings.

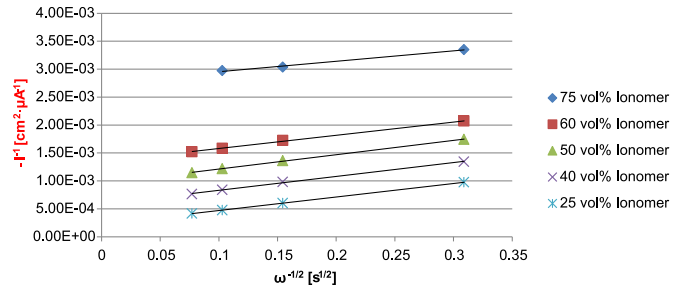


Fig. 6. Koutecky–Levich plots for different vol% anionomer contents for 75 µg Ag NW loadings.

where n is the number of electrons exchanged in the reaction for each oxygen molecule reduced, F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), A is the area of the GC electrode (0.19635 cm^2), D is the diffusion coefficient of O₂ in the 0.1 M KOH electrolyte ($2.10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) [24], ω is the rotation rate (measured in rad sec^{-1} , or simply s^{-1}), ν is the viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$) and C is the solubility of O₂ in the 0.1 M KOH electrolyte ($1.26 \times 10^{-6} \text{ mol cm}^{-3}$) [25]. The Levich equation is then modified with the addition of the kinetic limited current i_k in the following way:

$$\frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{0.62 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C} \quad (2)$$

thus giving the Koutecky–Levich equation. This can be simplified by using

$$B = 0.62 n F A D^{2/3} \nu^{-1/6} C \quad (3)$$

which is known as the Levich slope. Substituting the values for F , A , D and ν results in $B = (2.427 \times 10^{-5} \text{ s}^{1/2} \text{ A})n$, giving a simplified Koutecky–Levich equation:

$$\frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{B \omega^{1/2}} \quad (4)$$

In this simplified form, it can be readily seen that the diffusion limited current, which is measured at the disc electrode, is dependent upon the square root rotation rate $\omega^{1/2}$ in a linear relationship, with the slope given by B ; the kinetic limited current can then be found from the (extrapolated) y-intercept where a theoretical infinite rotation rate would overcome all diffusion limitations [2]. Thus, from the ORR polarization curves the inverse of the measured diffusion limited current density can be plotted against the inverse square root of the rotation rate to obtain the value for n . Fig. 6 shows an example of a Koutecky–Levich plot,

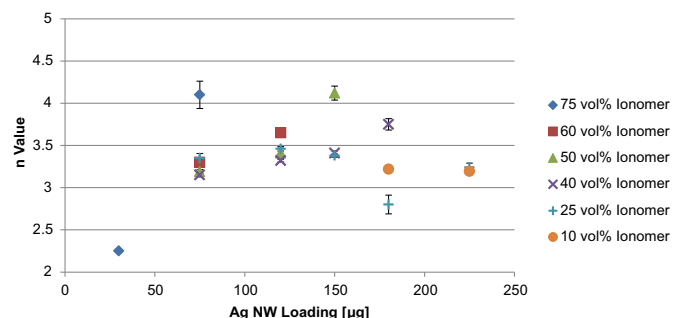


Fig. 7. n value versus Ag nanowire loading.

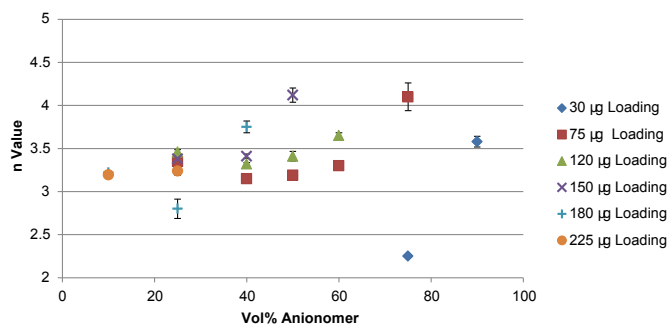


Fig. 8. n value versus vol% of anionomer solution in ink.

comparing the plots for various volume percentages of anionomer solution for a constant Ag nanowire loading of 75 μg .

Fig. 6 includes best linear fits, along with their associated linear equations. From the slopes of these linear fits it is then possible to determine their respective Levich slopes B , which can then be used for determining the average number of electrons exchanged for each O_2 molecule that is reduced. Assuming a value of 2 for n (i.e. assuming that the ORR proceeds entirely through the 2e^- path) results in a slope of approximately 0.004. In the case of ORR proceeding entirely through the 4e^- pathway the resulting slope is about 0.002. The slopes for all of the linear fits in Fig. 3 fall between these values, to within measurement error, indicating that with these catalysts ORR is proceeding through some combination of the 2e^- and 4e^- pathways. Furthermore, all of the slopes in this figure are all below 0.003, putting them closer to that associated with the 4e^- pathway than to that associated with the 2e^- pathway, indicating that ORR is proceeding primarily through the 4e^- pathway.

A more significant effect observed with the variation of the volume% of the anionomer solution in the deposited ink is the kinetic limited current i_k . As shown in Eq. (4), that the kinetic limited current is simply the inverse of the y-intercept of the linear equation. It can be seen from Fig. 3 that a lower volume% of anionomer solution in the deposited ink is associated with a lower y-intercept, corresponding to a higher kinetically-limited current. It is believed that this may be due to internal transport limitations introduced within the catalyst layer on the disc electrode as a result of high anionomer loading.

Although not shown in the figures, the n value was also calculated from the ORR polarization curves taken for the plain glassy carbon electrode, as well as for the GC electrode with 10 μl of anionomer solution deposited. The same was also done for 20 wt% Pt/C. For the former, an n value of 2.05 ± 0.07 was calculated, indicating ORR proceeding almost entirely through the 2-electron pathway, as would be expected for an uncoated GC electrode. For the anionomer deposited electrode, an n value of 1.3 ± 0.3 . This is somewhat lower than 2, but the greater error in the calculated value keeps this reasonably close to the value expected for the 2-electron pathway. In the case of the Pt/C sample, the calculated n value was found to be 4.49 ± 0.07 .

Collecting this data from Koutecky–Levich plots for the various loadings of Ag nanowires, it is then possible to look at how n varies with both Ag nanowire loading and anionomer content. Fig. 7 shows the variation of n with Ag nanowire loading for the inks with differing anionomer content. From the figure it appears that the value of n peaks is maximized between 75 and 150 μg of Ag nanowire loading.

In Fig. 8 the value of n is plotted against the anionomer content of the inks deposited with various constant loadings of Ag nanowires. Looking at this figure, a general trend can be seen, whereby there is an increase in the value of n with the increasing volume of anionomer solution in the deposited ink, which is to say that there appears to be a positive relation between the value of n and the amount of anionomer present. Thus it appears that an increase in the anionomer loading tends to promote the 4e^- ORR pathway over the 2e^- pathway, in spite of the fact that these very high loadings of ionomer appear to be causing internal transport limitations within the deposited catalyst layer, which tends to lower the overall current. This would indicate that the ionomer itself may play a role in the oxygen kinetics that take place at the electrode.

4. Conclusions

In summary, the impact of high loading of commercially available anionomer on ORR kinetics for silver nanowire catalysts in 0.1 M KOH electrolyte was investigated. By varying the volume ratio of the anionomer solution to the total volume of the ink (10, 25, 40, 50, and 75 vol%) it was possible to deposit constant loadings of Ag nanowire catalyst onto the GC electrode for use in RDE experiments. Using ORR polarization curves and Koutecky–Levich analysis, it was found that ORR tended to shift more towards the 4e^- pathway with increasing anionomer loadings. This indicates that silver-based catalyst systems may provide a cost-effective solution for emerging fuel cell and energy storage applications.

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